The effect of thermal vibrations on extended x-ray absorption fine structure. II

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A formalism is introduced to describe the dependence of the EXAFS amplitude and phase on thermally excited vibrations. The EXAFS expression for a general three-atom system of C_s symmetry is discussed in detail. To lowest order, thermal vibrations induce a change only in the scattering path length and give rise to the standard EXAFS expression for each scattering path damped by the appropriate Debye-Waller factor. A change in scattering angle, however, is a higher order effect and gives rise to additional EXAFS terms called modification factors. There is a modification factor associated with each multiple scattering path. Within this formalism, the correlation which exists between a change in scattering path length and a change in scattering angle is explicitly calculated. The normal modes which contribute to the modification factors are discussed, and shown to be dependent on the symmetry of the system. The nature and temperature dependence of the Debye–Waller and modification factors for the three-atom system Br_2O are discussed as a function of bridging angle. The modification factors are shown to make a small contribution to the total EXAFS of the system. The magnitude of this contribution is dependent on the degree of correlation that exists between changes in scattering path length and scattering angle.

I. INTRODUCTION

Extended x-ray absorption fine structure (EXAFS) refers to the modulations observed in the absorption coefficient on the high frequency side of an x-ray absorption edge. The origin of this structure was first explained by Kronig[1] who described the EXAFS in terms of a modification of the photoelectron's wave function due to the presence of neighboring atoms. Despite this early work, the potential of EXAFS to yield local structural information went unnoticed until Sayers, Stern, and Lytel[2] presented a parametrization of the extended structure in terms of physically significant quantities. Since then EXAFS has emerged as an important structural tool with applications in many areas of physics, chemistry, and biology.[3]

EXAFS yields structural information about the local environment of the atomic species which absorbs the x-ray photon. The modulations observed in the absorption coefficient are due to an interference phenomenon in which the outgoing photoelectron wave is scattered by neighboring atom potentials. The amplitude of the scattered wave returning to the absorption site is inversely proportional to the product of the individual scattering path lengths during which the photoelectron propagates freely. This ensures that the contribution to the EXAFS from distant shells is small. In addition, the limited coherent path length due to inelastic scattering and the finite lifetime of the core hole further serve to restrict the depth of penetration of the photoelectron into the bulk. Since multiple scattering events necessarily involve large path lengths this contribution to the EXAFS was generally considered to be small. Exception was taken to the case in which the absorbing atom and two neighboring atoms lined up such that the large forward scattering amplitude of the intervening atom compensated for the decrease in flux due to the long scattering path.[4] The short-range nature of the EXAFS effect thus facilitates an analysis of the extended structure. The predominance of single scattering and the relatively few distances involved make EXAFS amenable to the methods of Fourier analysis. The Fourier transform of an isolated EXAFS pattern yields a form of radial distribution function in which the central atom is located at the origin. The distribution function is distorted, however, due to the presence of phase shifts incurred by the photoelectron during the scattering process. From such an analysis it is possible to determine bond distances, coordination numbers, and the types of neighboring atoms involved.

Recently, however, there has been considerable interest in multiple scattering events in EXAFS. Teo[5] and Boland *et al.*[6] have shown that a three-atom system comprised of an absorbing atom and two neighboring atoms is sufficient to describe all significant multiple scattering effects. The amplitude and phase of the multiple scattering components were shown to be sensitive to the geometry of the system. When data analysis is based on a single scattering model, spectra which contain a significant degree of multiple scattering often appear to have anomalous Fourier coefficients. In such instances, however, a multiple scattering analysis should make possible a determination of the complete local geometry, including bond angles, about the absorbing atom. The frequency of the single and multiple scattering EXAFS components may be sufficiently similar that a Fourier analysis is unable to resolve the individual components. It is this problem which makes an accurate treatment of such EXAFS data difficult.

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To develop a method of analysis for multiple scattering EXAFS data it is necessary to understand the factors which affect the amplitude and phase of each EXAFS component. Teo[5] has suggested that the scattering paths involving the second shell atom may be combined and analyzed as though they described a single scattering process with a modified amplitude and phase. This method results in a considerable simplification of the data analysis. More recently, Alberding and Crozier[7] discussed separately the effects on the observed EXAFS of changes in bond distances and scattering angles. This present paper will address the problem of thermal vibrations and their effect on EXAFS spectra. In a previous paper[8] (subsequently to be referred to as I) we showed that, to lowest order, the Debye–Waller factor associated with changes in the internuclear distances may be treated separately from changes in scattering angles. The purpose of this present work is to describe the effects of changes in bond angles and the correlation that exists between such changes and the accompanying changes in bond distances.

II. FORMAL CONSIDERATION

To study the effects of thermal vibrations let us consider the general three-atom system shown in Fig. 1. Systems of this type have been discussed previously by Teo[5] and Boland *et al.*[6] In the absence of thermal vibrations the EXAFS for such a system may be described by

$$\chi^0(k,\hat{e}) = \chi_S^0(k,\hat{e}) + 2\chi_D^0(k,\hat{e}) + \chi_T^0(k,\hat{e}) . \tag{1}$$

The superscript zero indicates the absence of thermal vibrations and k is the photoelectron wave number defined by the free electron dispersion relation:

$$k = \left[\frac{2m}{\hbar^2}(\hbar\omega - E_0)\right]^{1/2} , \tag{2}$$

where $\hbar\omega$ is the energy of the x-ray photon and E_0 is the threshold energy. The subscripts S, D, and T refer to single, double, and triple scattering events and $\hat{e}$ is the unit vector which specifies the direction of polarization of the incident x-ray beam.

A schematic representaion of the scattering paths within this three-atom system is shown in Fig. 2. The single scattering EXAFS, $\chi_S^0(k,\hat{e})$, consists of two terms each of which corresponds to a single scattering event involving the neighboring atom located at $\mathbf{r} = \mathbf{r}_i$ or $\mathbf{r} = \mathbf{r}_j$. $\chi_S^0(k,\hat{e})$ may be expressed as

$$\chi_S^0(k,\hat{e}) = \sum_{g=i,j} \chi_{S_g}^0(k,\hat{e}) , \tag{3}$$

where

$$\chi_{S_g}^0(k,\hat{e}) = \frac{-3(\hat{r}_g\cdot\hat{e})^2}{kr_g^2} \operatorname{Im}\left[f_g(\pi,k) e^{2i\mathbf{k}_g\cdot\mathbf{r}_g} e^{2i\delta_1} \right] ,$$

where $\mathbf{k}_g = k\mathbf{r}_g$ and $\chi_{S_g}^0(k,\hat{e})$ represents the contribution to the total single scattering from atom g. The probability amplitude of atom g scattering the incident photoelectron through an angle π is given by $f_g(\pi,k)$. The double scattering EXAFS, $\chi_D^0(k,\hat{e})$, involves events in which the photoelectron successively scatters off one neighboring atom and then off the other remaining neighboring atom. By virtue of time reversal invariance the order in which this scattering sequence occurs does not affect the probability amplitude so that this term is counted twice in Eq. (1) [see Figs. 2(c) and 2(d)]. $\chi_D^0(k,\hat{e})$ may be written as

$$\chi_D^0(k,\hat{e}) = \frac{-3(\hat{r}_i\cdot\hat{e})(\hat{r}_j\cdot\hat{e})}{kr_ir_jr_{ij}} \operatorname{Im}\left\{ f_j(\alpha,k) f_j(\beta,k) e^{2i\delta_1} \times \exp\left[i(\mathbf{k}_j\cdot\mathbf{r}_j + \mathbf{k}_{ij}\cdot\mathbf{r}_{ij} + \mathbf{k}_i\cdot\mathbf{r}_i) \right] \right\} , \tag{4}$$

where $\mathbf{k}_{ij} = k\hat{r}_{ij} = k(\mathbf{r}_i - \mathbf{r}_j)/|\mathbf{r}_i - \mathbf{r}_j|$ and α and β are the scattering angles at atoms j and i, respectively. The triple scattering EXAFS term, $\chi_T^0(k,\hat{e})$, describes a process in which the outgoing photoelectron wave first scatters off the nearest neighboring atom j then scatters off atom i and finally scatters off atom j once again [see Fig. 2(e)]. $\chi_T^0(k,\hat{e})$ may be expressed as

$$\chi_T^0(k,\hat{e}) = \frac{-3(\hat{r}_j\cdot\hat{e})^2}{kr_j^2 r_{ij}^2} \operatorname{Im}\left\{ (f_j(\alpha,k))^2 f_i(\pi,k) e^{2i\delta_1} \times \exp 2i\mathbf{k}(\mathbf{k}_j\cdot\mathbf{r}_j + \mathbf{k}_{ij}\cdot\mathbf{r}_{ij}) \right\} . \tag{5}$$

To obtain an expression for the EXAFS corresponding to the configuration of the three atoms shown in [Fig. (1)] the relative equilibrium position vectors of the atoms must be replaced by their respective instantaneous position vectors.

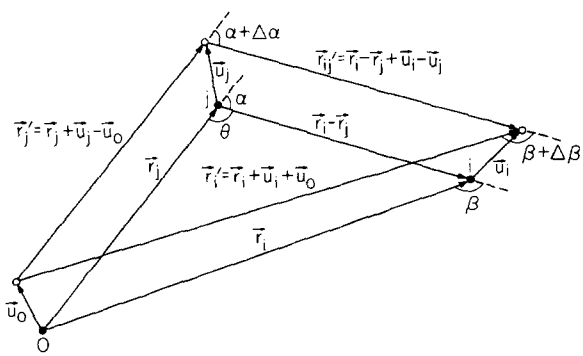


FIG. 1. The general three-atom system. The equilibrium positions of the central atom (o), first nearest-neighbor atom (j), and second nearest neighbor atom (i) are shown as filled circles. The displacement of these atoms from their respective equilibrium positions are shown as open circles. θ represents the equilibrium bridging angle. The equilibrium position of the central atom was chosen to represent the origin of the system.

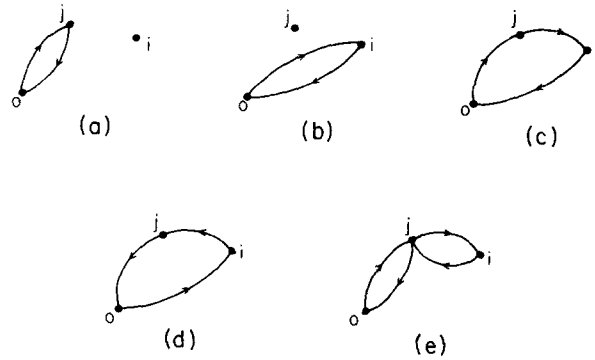


FIG. 2. The five significant scattering paths in a system of three atoms. (a) and (b) represent the single scattering paths from atoms i and j. The two double scattering paths (c) and (d) are identical by virtue of time-reversal symmetry. The triple scattering path is shown in (e).

The EXAFS is then described in terms of the instantaneous bond angles and distances of the system. To describe the effect such configurations have on the observed EXAFS spectrum, it is necessary to express the instantaneous value of any factor in terms of its equilibrium value together with a time dependent expression describing the deviation of this factor from equilibrium. Consideration of Eqs. (3) through (5) shows that there are four such factors, common to all equations, which are sensitive to the instantaneous geometry of the system. We shall now identify and estimate the importance of each of these four factors.

First let us consider the polarization terms which are common to all EXAFS expressions. Note that there are essentially two types of polarization factors. The instantaneous values of these dot products may be expressed in terms of their equilibrium values by expanding the products in a Taylor series. Since we are primarily concerned with polycrystalline samples these dot products must be averaged over all possible polarization directions. It may be shown that to first order, changes in the position vectors of the atoms do not effect the spherically averaged polarization factor. These factors will not be discussed further; to the order of the present calculations they are sufficiently well approximated by their equilibrium values. When single crystals or directionally oriented samples (e.g., surfaces) are being studied, however, it is necessary to calculate explicitly each of the terms in Taylor series.

The second factor to be considered is the exponential term representing the total scattering path length. Since each term of this type is similar we shall focus on a given term and generalize the results. In single scattering events involving atom j the exponential term in Eq. (3) corresponding to the instantaneous configuration shown in Fig. 1 may be written as

$$e^{2i\mathbf{k}_j'\cdot\mathbf{r}_j'} = \exp(2ik\,|\mathbf{r}_j + \mathbf{u}_j - \mathbf{u}_0|)\,, \tag{6}$$

where $\mathbf{k}_j' = k\hat{r}_j'$ and $\mathbf{r}_j'$ is the instantaneous position vector corresponding to the equilibrium position vector $\mathbf{r}_j$. The displacement vectors of the central atom and atom j are given by $\mathbf{u}_0$ and $\mathbf{u}_j$, respectively. The path length may be written as

$$|\mathbf{r}_j + \mathbf{u}_j - \mathbf{u}_0| = (r_j^2 + u_j^2 + u_0^2 + 2\mathbf{r}_j\cdot\mathbf{u}_j - 2\mathbf{r}_j\cdot\mathbf{u}_0 - 2\mathbf{u}_j\cdot\mathbf{u}_0)^{1/2}\,. \tag{7}$$

Retaining only the lowest order terms in the displacement, this distance may be approximated as follows:

$$|\mathbf{r}_j + \mathbf{u}_j - \mathbf{u}_0| \simeq r_j\,[1 + 2\hat{r}_j\cdot(\mathbf{u}_j - \mathbf{u}_0)/r_j\,]^{1/2} \approx r_j + \hat{r}_j\cdot(\mathbf{u}_j - \mathbf{u}_0)\,. \tag{8}$$

Substituting Eq. (8) into Eq. (6) reveals that the original exponential term is factored into the equilibrium separation of the atoms and the projection of the displacement vectors along the bond defined by these atoms.

$$\exp(2ik\,|\mathbf{r}_j + \mathbf{u}_j - \mathbf{u}_0) = e^{2ikr_j}\exp[\,2ik\hat{r}_j\cdot(\mathbf{u}_j - \mathbf{u}_0)\,]\,. \tag{9}$$

A similar treatment may be applied to the remaining terms of this type.

The next quantity which must be discussed in our treatment of thermal vibrations is the effect of the instantaneous distances which occur in the denominator each EXAFS component. Using the approximations developed above in Eq. (8) it may be shown that such terms are negligible and we may replace the instantaneous distances in the denominator by their equilibrium values.

The remaining factor to be considered is the effect on the scattering amplitude of small changes in the directions of the incident and scattered photoelectron wave induced by thermal vibrations. The instantaneous scattering amplitude of atom j may be expressed in a Taylor series about the equilibrium scattering angle α:

$$f_j(\alpha + \Delta\alpha, k) = f_j(\alpha, k) = \left(\frac{\partial f_j(\alpha', k)}{\partial \alpha'}\right)_\alpha \Delta\alpha + O(\Delta\alpha^2)\,, \tag{10}$$

where $\Delta\alpha$ is the deviation from the equilibrium value. Note that in instances where the equilibrium scattering angle is π, the instantaneous angle is also π so that single scattering events need not be considered further.

To estimate the magnitude of the lowest order term in Eq. (10) it is necessary to express the angular deviation in terms of the displacement vectors of the three atoms shown in Fig. 1. The scattering angle may be written in terms of the unit vectors of the system

$$\cos\alpha = \hat{r}_j\cdot\hat{r}_{ij}\,. \tag{11}$$

Equation (11) may be differentiated to yield

$$\Delta\cos\alpha = -\sin\alpha\Delta\alpha = \hat{r}_j\cdot\Delta\hat{r}_{ij} + \Delta\hat{r}_j\cdot\hat{r}_{ij}\,, \tag{12}$$

so that the change in the angle from its equilibrium value is given by

$$\Delta\alpha = -\frac{\hat{r}_j\cdot\Delta\hat{r}_{ij} + \Delta\hat{r}_j\cdot\hat{r}_{ij}}{\sin\alpha}\,. \tag{13}$$

Noting that each unit vector may be written as $\hat{\mathbf{r}}_j = \mathbf{r}_j/r_j$, an expression for the deviation in angle may be readily obtained. Separating the contribution to $\Delta\alpha$ from each of the displacement vectors allows Eq. (13) to be written in the form

$$\Delta\alpha = \mathbf{a}_j\cdot\mathbf{u}_0 + \mathbf{b}_j\cdot\mathbf{u}_i + \mathbf{c}_j\cdot\mathbf{u}_j\,,$$

where

$$\mathbf{a}_j = \frac{\hat{r}_{ij} - \hat{r}_j\cos\alpha}{r_j\sin\alpha}\,,$$

$$\mathbf{b}_j = \frac{\hat{r}_{ij}\cos\alpha - \hat{r}_j}{r_{ij}\sin\alpha}\,,$$

$$\mathbf{c}_j = \frac{r_j(\hat{r}_j - \hat{r}_{ij}\cos\alpha) + r_{ij}(\hat{r}_j\cos\alpha - \hat{r}_{ij})}{r_j r_{ij}\sin\alpha}\,. \tag{14}$$

It is important to note that the vectors a_j, b_j, and c_j are functions only of the equilibrium geometry of the three atom system. An expression of this type also exists for $\Delta\beta$, the deviation in the scattering angle about atom i, in which

$$\mathbf{a}_i = -\frac{\hat{r}_{ij} + r_i\cos\beta}{r_i\sin\beta}\,,$$

$$\mathbf{b}_i = \frac{r_i(\hat{r}_i + \hat{r}_{ij}\cos\beta) + r_{ij}(\hat{r}_{ij} + \hat{r}_{ij}\cos\beta)}{r_i r_{ij}\sin\beta}\,,$$

$$\mathbf{c}_i = -\frac{\hat{r}_i + \hat{r}_{ij}\cos\beta}{r_{ij}\sin\beta}\,. \tag{15}$$

III. EXAFS MODIFICATION FACTORS

Our discussion of the significance of the four factors present in each EXAFS component is now complete. These factors represent the possible ways in which thermal vibrations may modify EXAFS spectra. With the above information in hand we may write out in detail an expression for the EXAFS due to the instantaneous configuration shown in Fig. 1. To obtain the experimentlly observed EXAFS, however, we must perform an ensemble average of this expression over the canonical ensemble defined by the Hamiltonian of the three-atom system. Retaining only the lowest order terms in the angular displacement, this ensemble average may be written as:

$$\begin{aligned}\langle\chi(k,\hat{e})\rangle = {} & \chi_S^0\langle\exp[2ik\hat{r}_g(\mathbf{u}_g-\mathbf{u}_0)]\rangle + 2\chi_D^0\langle\exp\{ik\,[\hat{r}_j\cdot(\mathbf{u}_j-\mathbf{u}_0)+\hat{r}_{ij}\cdot(\mathbf{u}_i-\mathbf{u}_j)]\}\\ & \times\exp\{ik\,[\hat{r}_i\cdot(\mathbf{u}_i-\mathbf{u}_0)]\}\rangle + \chi_T^0\,\langle\exp\{2ik\,[\hat{r}_j\cdot(\mathbf{u}_j-\mathbf{u}_0)+\hat{r}_{ij}\cdot(\mathbf{u}_i-\mathbf{u}_j)]\}\rangle\\ & -\frac{6(\hat{r}_j\cdot\hat{e})(\hat{r}_i\cdot\hat{e})}{kr_i\,r_j\,r_{ij}}\,\mathrm{Im}\left(f_i(\beta,k)\left(\frac{\partial f_j(\alpha',k)}{\partial\alpha'}\right)_\alpha\exp[ik(r_j+r_{ij}+r_i)]\,e^{2i\delta_1}\right.\\ & \left.\times\langle\Delta\alpha\exp\{ik\,[\hat{r}_j\cdot(\mathbf{u}_j-\mathbf{u}_0)+\hat{r}_{ij}\cdot(\mathbf{u}_i-\mathbf{u}_j)+\hat{r}_i\cdot(\mathbf{u}_i-\mathbf{u}_0)]\}\rangle\right)\\ & -\frac{6(\hat{r}_j\cdot\hat{e})(\hat{r}_i\cdot\hat{e})}{kr_i\,r_j\,r_{ij}}\,\mathrm{Im}\left(f_j(\alpha,k)\left(\frac{\partial f_i(\beta',k)}{\partial\beta'}\right)_\beta\exp[ik(r_j+r_{ij}+r_i)]\,e^{2i\delta_1}\right.\\ & \left.\times\,\langle\Delta\beta\exp\{ik\,[\hat{r}_j\cdot(\mathbf{u}_j-\mathbf{u}_0)+\hat{r}_{ij}\cdot(\mathbf{u}_i-\mathbf{u}_j)+\hat{r}_i\cdot(\mathbf{u}_i-\mathbf{u}_0)]\}\rangle\right)\\ & -\frac{6(\hat{r}_j\cdot\hat{e})^2}{kr_j^2\,r_{ij}^2}\,\mathrm{Im}\left(f_i(\pi,k)f_j(\alpha,k)\left(\frac{\partial f_j(\alpha',k)}{\partial\alpha'}\right)_\alpha\exp[2ik(r_j+r_{ij})]\right.\\ & \left.\times e^{2i\delta_1}\,\langle\Delta\alpha\exp\{2ik\,[\hat{r}_j\cdot(\mathbf{u}_j-\mathbf{u}_0)+\hat{r}_{ij}(\mathbf{u}_i-\mathbf{u}_j)]\}\rangle\right),\end{aligned} \tag{16}$$

where the brackets $\langle\cdots\rangle$ denote the ensemble or thermal average of the quantity enclosed. The first three terms in Eq. (16) above correspond to the case in which the only contribution to the Debye–Waller factor is due to changes in the interatomic distances. Note that these terms are described by the usual type of Debye–Waller factor in which the EXAFS expression in the absence of vibrations is multiplied by a damping term to account for the effects of thermal vibrations. These terms have been discussed previously in I and they will not be discussed further in this present work. The remaining terms represent the combined effect of changes in both angles and distances. These variations are strongly correlated and this fact must be taken into account when the appropriate thermal averages are performed. Note that these latter terms involve only the double and triple EXAFS components. Since these terms must be added to the damped EXAFS expression defined by the first three terms in Eq. (16), it is inappropriate to refer to these terms as Debye–Waller factors. For the purpose of the present discussion, we shall call such terms modification factors, since each has a modified amplitude and phase when compared to the corresponding term in the damped EXAFS expression. An amplitude modification occurs due to the presence, in each of these factors, of a derivative of the scattering amplitude together with an angular variation term in the thermal average. The phase of each factor is modified because the phase of a derivative of the scattering amplitude may be different from the phase of the amplitude itself.

We shall now focus attention on the thermal averages which occur within each modification factor. To calculate explicitly such averages, it is necessary to know the potential energy surface governing the motion of the three-atom system. Throughout this work the harmonic or quadratic approximation is assumed. This approximation consists of expanding the potential energy in a Taylor series about its equilibrium value and truncating the expansion after the first nonzero term. This is consistent with our expansion of the scattering amplitudes about the equilibrium scattering angle in which only the first order term was retained. Each of these approximations is then strictly valid only for small departures from equilibrium. Therefore, it is possible to approximate Eq. (14) by

$$\Delta\alpha = \frac{1}{2i}\{\exp[i(\mathbf{a}_j\cdot\mathbf{u}_0+\mathbf{b}_j\cdot\mathbf{u}_i+\mathbf{c}_j\cdot\mathbf{u}_j)] - \exp[-i(\mathbf{a}_j\cdot\mathbf{u}_0+\mathbf{b}_j\cdot\mathbf{u}_i+\mathbf{c}_j\cdot\mathbf{u}_j)]\}\,. \tag{17}$$

A similar expression may be obtained for $\Delta\beta$.

Since the form of the potential energy surface is harmonic it is convenient to express the displacement vectors in terms of the normal coordinates $Q_n (n = 1,\ldots,3N)$,

$$\mathbf{u}_j = \sum_n \mathbf{e}_j^n\,Q_n\,, \tag{18}$$

where N is the number of atoms in the system and $\mathbf{e}_j^n$ is the amplitude vector of the jth atom in the nth normal mode. The properties and advantages of this coordinate system have been discussed in I. In the case of our three atom system there is a total of nine degrees of freedom so that the sum over n above extends to three terms for the nonlinear systems

and four terms for linear systems. The remaining terms represent translation and rotation of the system as a whole and do not contribute to the EXAFS. For harmonic systems it may be shown that[9]

$$\langle e^{if(n)Q_n}\rangle = \exp -\tfrac{1}{2}\,[f(n)]^2\langle Q_n^2\rangle\,, \tag{19}$$

where $f(n)$ is some function of the normal mode n and $\langle Q_n^2\rangle$ is the mean-square amplitude of vibration in the nth normal mode. Furthermore, $\langle Q_n^2\rangle$ may be written as[10]

$$\langle Q_n^2\rangle = \frac{\hbar}{2\omega_n}\coth\left(\frac{\hbar\omega_n}{2k_BT}\right), \tag{20}$$

where ω_n is the frequency of the nth normal mode and k_B is Boltzmann's constant.

The explicit form of the thermal averages may now be determined. For convenience of notation let us define $\langle\Delta\alpha\rangle_D$ to be the thermal average that occurs within the double scattering modification factor in which the angle α changes by $\Delta\alpha$. Substituting Eq. (18) into Eq. (17) and then into the appropriate term in Eq. (16) an expression for $\langle\Delta\alpha\rangle_D$ is obtained:

$$\langle\Delta\alpha\rangle_D = \frac{1}{2i}\left\langle\exp\left\{ik\sum_n\left[(\mu_{j0}^n+\mu_{ij}^n+\mu_{i0}^n)+\frac{1}{k}(\rho_{j0}^n+\rho_{ji}^n+\rho_{jj}^n)\right]Q_n\right\}\right\rangle$$
$$-\frac{1}{2i}\left\langle\exp\left\{ik\sum_n\left[(\mu_{j0}^n+\mu_{ij}^n+\mu_{i0}^n)-\frac{1}{k}(\rho_{j0}^n+\rho_{ji}^n+\rho_{ij}^n)\right]Q_n\right\}\right\rangle. \tag{21}$$

In the preceding equation, $\mu_{ij}^n = \hat{r}_{ij}\cdot(\mathbf{e}_i^n - \mathbf{e}_j^n)$ and represents the maximum effective change in the distance along the internuclear axis between atoms i and j in the nth normal mode. The contribution to the change in the scattering angle at atom i due to the displacement of atom j in the nth normal mode is given by $\rho_{ij}^n = \mathbf{c}_i\cdot\mathbf{e}_j^n$. A similar interpretation applies to the remaining terms of these types. Note that each of the two terms in Eq. (21) contains a summation in the exponent which may be replaced by a product of exponential terms. This product extends over all of the normal modes of the system. Since there is no correlation between the individual normal modes the average of each product is just the product of the averages. Using Eq. (19) we can determine the thermal average associated with each normal mode in Eq. (21), calculate the product of these averages and thus determine $\langle\Delta\alpha\rangle_D$.

$$\langle\Delta\alpha\rangle_D = i\exp\left[-\tfrac{1}{2}k^2\sum_n(\mu_{j0}^n+\mu_{ij}^n+\mu_{i0}^n)^2\langle Q_n^2\rangle\right]\exp\left[-\tfrac{1}{2}\sum_n(\rho_{j0}^n+\rho_{ji}^n+\rho_{jj}^n)^2\langle Q_n^2\rangle\right]$$
$$\times\sinh\left[k\sum_n(\mu_{j0}^n+\mu_{ij}^n+\mu_{i0}^n)(\rho_{j0}^n+\rho_{ji}^n+\rho_{jj}^n)\langle Q_n^2\rangle\right]. \tag{22}$$

The remaining thermal averages $\langle\Delta\beta\rangle_D$ and $\langle\Delta\beta\rangle_T$, may be determined in a similar fashion.

Several features of this equation deserve comment. Equation (22) has been written in a manner which emphasizes the individual contributions to the thermal average due to changes in bond lengths and scattering angles. Note that the magnitude of the exponential damping term involving a change in scattering angle is not dependent on the energy of the photoelectron. The hyperbolic sine term represents the fact that there is a correlation between a change in bond length and a change in scattering angle. Note also that the thermal average is a pure imaginary quantity; this has the effect of shifting the phase of the EXAFS oscillations due to the modification factors by $\pi/2$. Therefore the sine wave oscillations of the original EXAFS take the form of a cosine wave in the modification factors.

It is now possible to write down a complete expression for the thermally averaged modification factors in Eq. (16),

$$\langle\chi_M(k,\hat{e})\rangle = \frac{-6(\hat{r}_j\cdot\hat{e})(\hat{r}_i\cdot\hat{e})}{kr_i\,r_j\,r_{ij}}\exp\left(-\tfrac{1}{2}k^2\sum_n(\mu_{j0}^n+\mu_{ij}^n+\mu_{i0}^n)^2\langle Q_n^2\rangle\right)\times\exp\left[-\tfrac{1}{2}\sum_n(\rho_{j0}^n+\rho_{ji}^n+\rho_{jj}^n)^2\langle Q_n^2\rangle\right]$$
$$\times\sinh\left[k\sum_n(\mu_{j0}^n+\mu_{ij}^n+\mu_{ij}^n)(\rho_{j0}^n+\rho_{ji}^n+\rho_{jj}^n)\langle Q_n^2\rangle\right]$$
$$\times\,\mathrm{Re}\left\{f_i(\beta,k)\left(\frac{\partial f_j(\alpha',k)}{\partial\alpha'}\right)_\alpha\exp[ik(r_j+r_{ij}+r_i)]\,e^{2i\delta_1}\right\}$$
$$\times\frac{-6(\hat{r}_j\cdot\hat{e})(\hat{r}_i\cdot\hat{e})}{kr_i\,r_j\,r_{ij}}\exp\left[-\tfrac{1}{2}k^2\sum_n(\mu_{j0}^n+\mu_{ij}^n+\mu_{i0}^n)^2\langle Q_n^2\rangle\right]$$
$$\times\exp\left[-\tfrac{1}{2}\sum_n(\rho_{i0}^n+\rho_{ii}^n+\rho_{ij}^n)^2\right]\langle Q_n^2\rangle\sinh\left[k\sum_n(\mu_{j0}^n+\mu_{ij}^n+\mu_{i0}^n)(\rho_{i0}^n+\rho_{ii}^n+\rho_{ij}^n)\langle Q_n^2\rangle\right]$$
$$\times\mathrm{Re}\left\{f_j(\alpha,k)\left(\frac{\partial f_i(\beta',k)}{\partial\beta'}\right)_\beta\exp[ik(r_j+r_{ij}+r_i)]\,e^{2i\delta_1}\right\}\frac{-6(\hat{r}_j\cdot\hat{e})^2}{kr_j^2r_{ij}^2}\exp\left[-2k^2\sum_n(\mu_{j0}^n+\mu_{ij}^n)^2\langle Q_n^2\rangle\right]$$
$$\times\exp\left[-\tfrac{1}{2}\sum_n(\rho_{j0}^n+\rho_{ji}^n+\rho_{jj}^n)^2\langle Q_n^2\rangle\right]\sinh\left[2k\sum_n(\mu_{j0}^n+\mu_{ij}^n)(\rho_{j0}^n+\rho_{ji}^n+\rho_{jj}^n)\langle Q_n^2\rangle\right]$$
$$\times\mathrm{Re}\left\{f_i(\pi,k)f_j(\alpha,k)\left(\frac{\partial f_j(\alpha',k)}{\partial\alpha'}\right)_\alpha\exp[2ik(r_j+r_{ij})]\,e^{2i\delta_1}\right\}. \tag{23}$$

The subscript M refers to that fact that Eq. (23) represents only the modified portion of the total EXAFS expression given in Eq. (16) for a general three-atom system of C_S symmetry.

IV. APPLICATION TO MODEL SYSTEMS

A series of model systems will be considered to determine the contribution of the modification factors in Eq. (23) to the observed EXAFS. To illustrate the symmetry properties of these factors let us consider a three-atom system which is symmetric and bent with a bridging angle $\theta = \pi - \alpha$. A plane of symmetry of the molecule passes through atom j such that the central atom (0) and the second nearest neighbor (i) are of the same type. This system then belongs to the C_{2v} point group and the normal modes of vibration transform as

$$\Gamma_{\text{vib}} = 2A_1 + B_1 . \tag{24}$$

The two totally symmetric A_1 modes correspond to a symmetric stretching and bending mode of vibration. The single B_1 mode is associated with the asymmetric stretch. A schematic representation of the normal modes of the three-atom system is shown in Fig. 3.

The symmetry of the system allows us to simplify the modification factors in Eq. (23). All modes in a C_{2v} point group are subject to the following conditions:

$$\begin{array}{ll} \text{For all modes in the} & m_0 = m_i = m \\ C_{2v} \text{ point group:} & |\mathbf{e}_0^n| = |\mathbf{e}_i^n| \end{array} , \tag{25}$$

where m_0 and m_i are the masses of the central atom and neighboring atom i, respectively. The symmetry properties of the terms μ_{ij}^n has been discussed fully in I. In this present work we shall only consider the additional symmetry properties due to the terms ρ_{ij}^n. The properties of these latter terms, however, depend on the symmetry properties of the vectors **a**, **b**, and **c** in Eqs. (14) and (15). Note that for any system

$$\mathbf{a}_t + \mathbf{b}_t + \mathbf{c}_t = 0 , \quad t = i, j , \tag{26}$$

which represents the requirement that the center of mass is fixed during a pure vibration. The symmetry properties of ρ_{ij}^n are also dependent on the normal mode in question and the atom at which the scattering angles varies.

We shall consider first the case in which the angular variation occurs at atom j. For a symmetric system of the type being discussed Fig. 4 shows that $\mathbf{c}_j$ bisects the bridging angle θ in all normal modes. Furthermore, $\mathbf{a}_j$ and $\mathbf{b}_j$ are equal in magnitude and the angle between them is also bisected by $\mathbf{c}_j$. Therefore, all A_1 type modes satisfy the following conditions (see Fig. 3):

$$\mathbf{a}_j \cdot \mathbf{e}_0^{A_1} = \mathbf{b}_j \cdot \mathbf{e}_i^{A_1}$$

or

$$\rho_{j_0}^{A_1} = \rho_{ji}^{A_1} ; \tag{27}$$

A_1 modes:

$$\mathbf{c}_j \cdot \mathbf{e}_j^{A_1} = \pm |\mathbf{c}_j| \, |\mathbf{e}_j^{A_1}| = \rho_{jj}^{A_1} .$$

The first part of Eq. (27) expresses the fact that displacement of atom i and the central atom in an A_1 mode produce the same change in the scattering angle at atom j. The sign of the second part of this equation is determined by whether the mode is a bend or a stretch. In the single B_1 mode, however, the contribution to the change in angle α due to the displacements of the central atom and atom i cancel exactly. In addition, $\mathbf{c}_j$ is perpendicular to $\mathbf{e}_j^{B_1}$ so that the following conditions must be satisfied:

$$B_1 \text{ mode:} \begin{array}{l} \rho_{j0}^{B_1} = -\rho_{ji}^{B_1} \\ \mathbf{c}_j \cdot \mathbf{e}_j^{B_1} = \rho_{jj}^{B_1} = 0 \end{array} . \tag{28}$$

Thus the B_1 mode does not contribute to a change in the scattering angle α.

No symmetry arguments may be applied to the modification factor which involves a change in the scattering angle β. This is because no symmetry element, other than the plane of the system, maps atom i onto itself. To determine this modification factor it is necessary to calculate explicitly all of the terms shown in Eq. (23).

There are essentially two separate calculations necessary to determine the modification factors in Eq. (23). The first involves a calculation of the experimental and hyperbo-

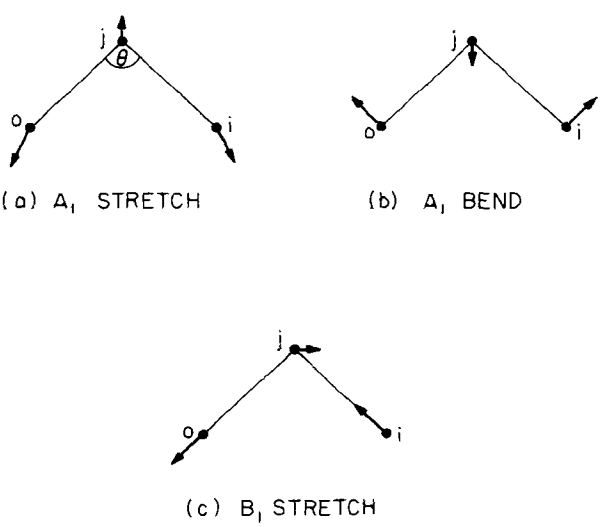


FIG. 3. Schematic of the normal modes in a three-atom system of C_{2v} symmetry. There are three normal modes, two of A_1 type symmetry and a single B_1 mode.

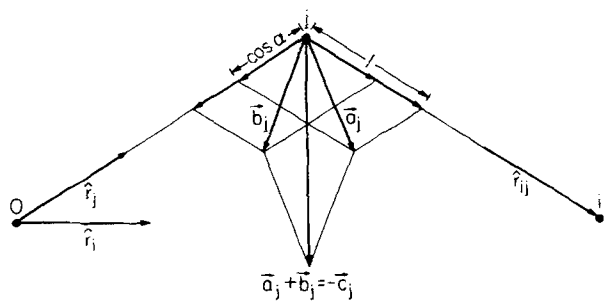


FIG. 4. Schematic representation of the vectors which determine the change in scattering angle α at atom j due to the displacement of all the atoms in a given normal mode [see Eq. (23)].

lic sine terms and requires a full normal mode analysis of the system. The details, and the manner in which such an analysis may be performed has been discussed in I. The second calculation requires a determination of the contribution of the scattering amplitude and phase of the modification factors. This latter calculation requires a knowledge of the modulus and phase of the scattering amplitudes as a function of scattering angle and wave number k. Assuming a plane wave approximation the scattering amplitude may be written as

$$f_j(\alpha,k) = F_j(\alpha,k)e^{i\phi(\alpha,k)}, \tag{29}$$

where $F_j(\alpha,k)$ is the modulus of the scattering amplitude and $\phi(\alpha,k)$ is the phase of the amplitude. This approximation is valid for large bond distances or small scattering atoms. The derivatives in Eq. (23) now take the form:

$$\left(\frac{\partial f_j(\alpha',k)}{\partial\alpha'}\right)_\alpha = e^{i\phi(\alpha,k)}\left(\frac{F_j(\alpha',k)}{\partial\alpha'}\right)_\alpha + F_j(\alpha,k)\left(\frac{\partial e^{i\phi(\alpha',k)}}{\partial\alpha'}\right)_\alpha . \tag{30}$$

Values of the modulus and phase of the scattering amplitude as a function of the scattering angle have been reported only for carbon and oxygen atoms.[11] Since we are concerned with bridged systems in which the central atom and atom i are heavy atoms we have insufficient information to calculate the modification factors in Eq. (23). However, Teo[5] has shown that the scattering amplitude at atom i may be approximated by

$$f_i = (\beta,k) = f_i(\pi,k), \quad 120° \leqslant \beta \leqslant 180°, \tag{31}$$

which includes the angular range in which multiple scattering is most likely to be important. In this approximation, the rate of change of the scattering amplitude at atom i with respect to the scattering angle β is zero. Therefore, the modification factor involving a change in this angle β is also zero. Equation (23) then reduces to two terms corresponding to the double and triple scattering modification factors in which angle α changes by $\Delta\alpha$. In the case of heavy elements, structure tends to be developed in the angular range of Eq. (31) making the validity of this approximation questionable.[5] Despite this, we shall assume Eq. (31) to be valid since no information exists on the angular dependence of the scattering amplitudes for such elements.

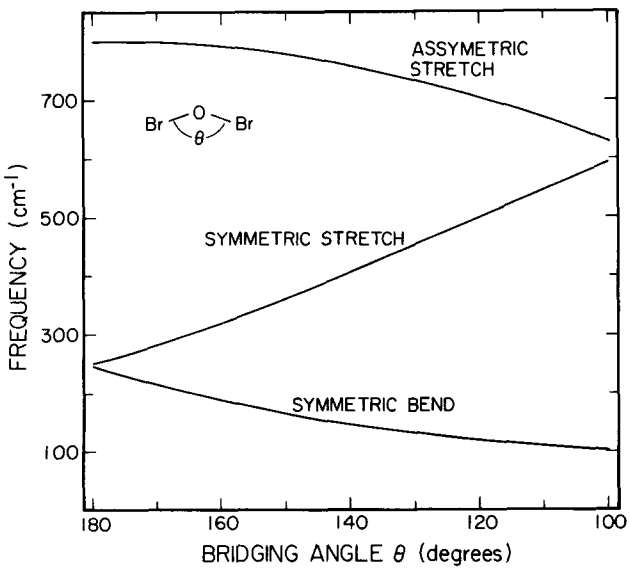


FIG. 5. Calculated frequencies of the normal modes of vibration for the Br_2O system as a function of bridging angle θ.

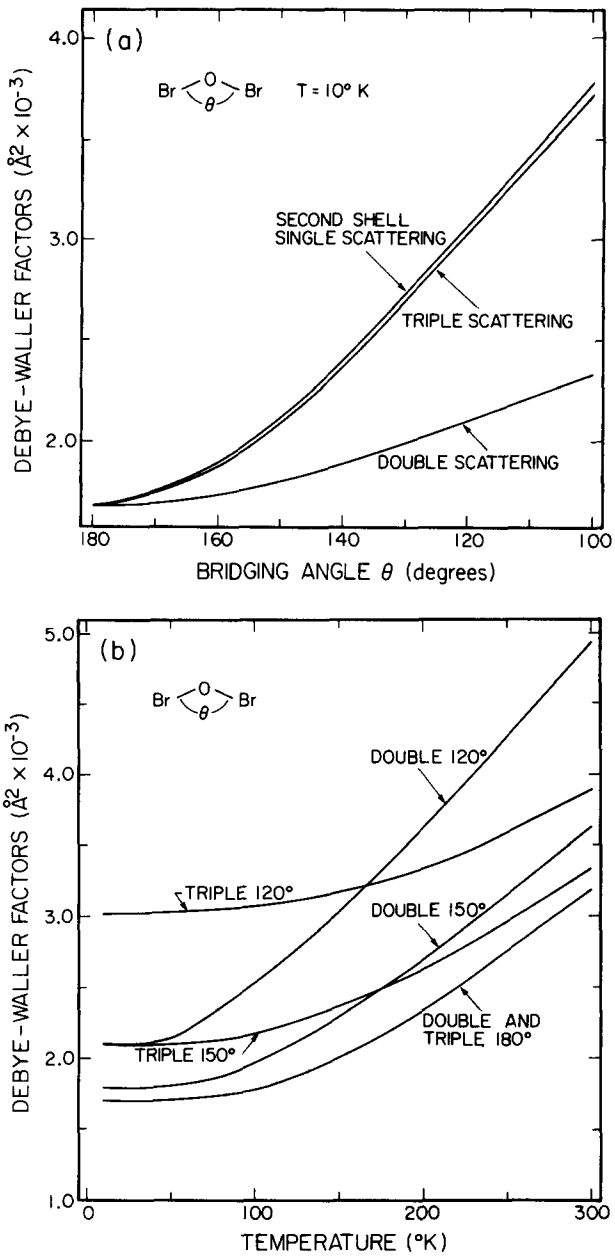


FIG. 6. Debye–Waller factors for the three-atom system. (a) Debye–Waller factor as a function of bridging angle at 10 K. (b) Debye–Waller factor as a function of temperature for bridging angles 120°, 150°, and 180°.

The model system to be studied is Br_2O, which we shall consider to be representative of oxygen bridged systems. We shall assume that the symmetric stretch and bend occur at 250 and 245 cm^{-1} in the linear system while the asymmetric stretch occurs at 800 cm^{-1}. The normal frequencies of the linear bridged system are then used to generate a set of force constants as described in I. These force constants are assumed to be independent of the geometry of the molecule and are used to calculate the normal frequencies at any

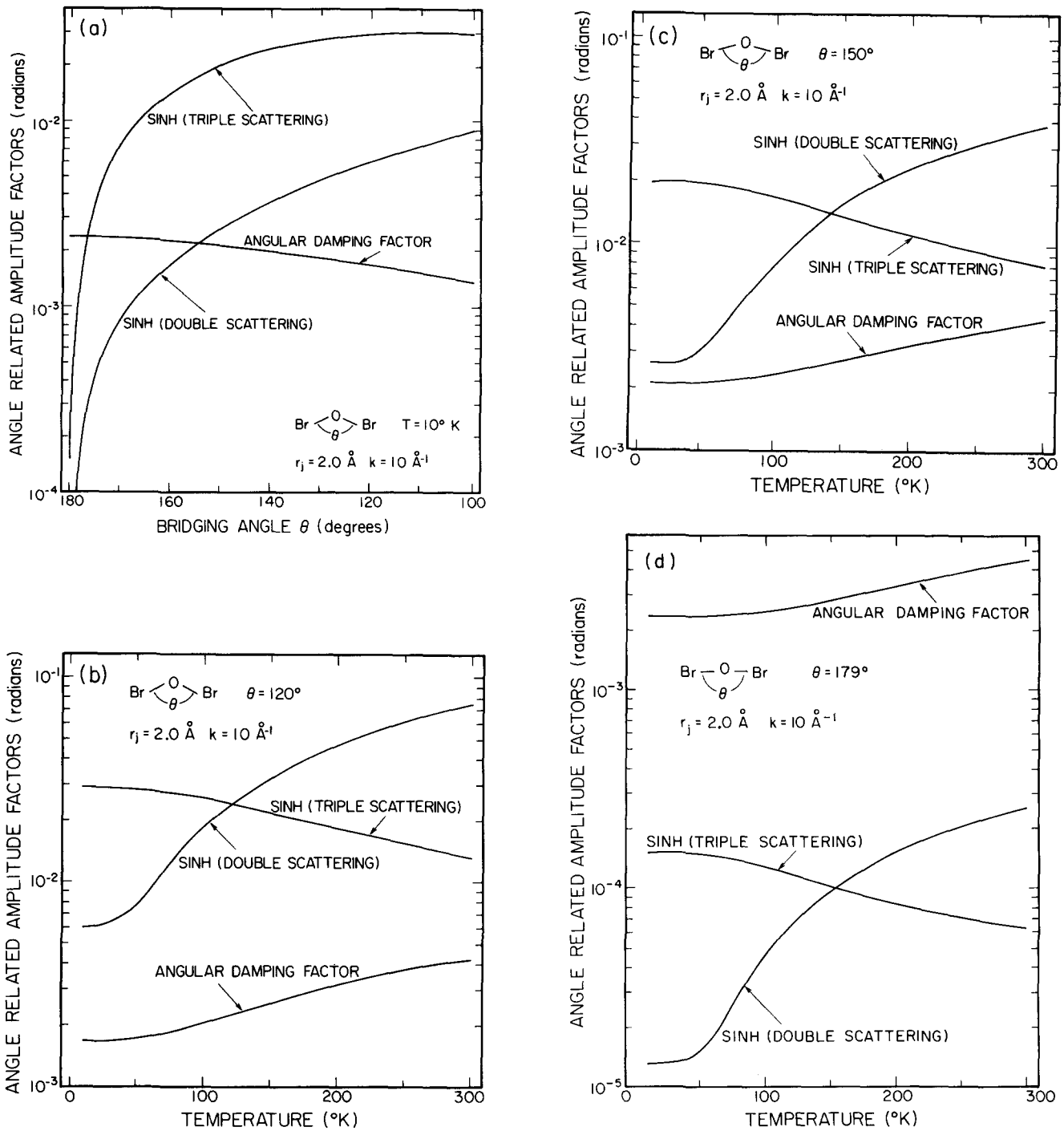


FIG. 7. The argument of the hyperbolic sine terms for the double and triple scattering paths [see Eq. (33)]. The angular damping factor is the exponent of the exponential term which represents the damping of the EXAFS due to a change in the scattering angle α. The hyperbolic sine terms were calculated at $k = 10$ Å^{-1} and a bond distance of 2.0 Å was used throughout. Note that the sign of the double scattering hyperbolic term is negative. (a) These terms as a function of bridging angle at 10 K. (b) As a function of temperature at a bridging angle of 120°, (c) 150°, (d) 179°.

bridging angle θ. This assumption is least valid for a description of the bending mode of vibration. The frequencies chosen above are typical of those found in linear oxygen bridged systems.[12]

The calculated frequency of each of the normal modes as a function of bridging angle is shown in Fig. 5. The angular despersion of the normal frequencies agrees well with earlier calculations and observations of oxygen bridged systems.[12] The calculated Debye–Waller factors and angle-related amplitude factors are shown in Figs. 6 and 7, respectively. The modulus and phase of the scattering amplitudes together with their derivatives are shown in Figs. 8 and 9. Finally, Figs. 10 and 11 illustrate the angle and temperature dependence of the amplitude of the EXAFS corresponding to each scattering path including the associated modification factors.

V. DISCUSSION

We have presented a general description of the effect of thermal vibrations on extended x-ray absorption fine structure. The formalism developed is general and may be applied to any scattering problem in which there exists a correlation between a change in distance and a change in scattering angle. An expression was obtained for the EXAFS in a general three-atom system of C_S symmetry. Variation in the scattering angle was shown to give rise to additional EXAFS terms which we called modification factors. The form of these modification factors was shown to be dependent on the geometry and symmetry of the system. The formalism, in its present form, is readily applicable to multiple scattering events involving more than three atoms. Systems of the other than C_{2v} symmetry may be considered by determining the symmetry properties of the Debye–Waller and modification factors subject to the point group in question.

The Debye–Waller factors which reflect the damping of the EXAFS amplitude due to thermally induced changes in the internuclear distances of the system are shown in Fig. 6. The double scattering factor in Fig. 6 has been divided by four such that the Debye–Waller factors associated with each scattering path have the standard form $\exp(-2k^2\sigma^2)$ [see Eq. (23)]. It is important to note that there are two quantities which determine the contribution of a given normal mode to the Debye–Waller factor for a particular scattering path. The frequency of the normal mode determines the mean square amplitude of vibration in accordance with Eq. (20). In addition, the amplitude and direction of the displacement vectors of the atoms in a given normal mode determine the projection of these vectors along the internuclear axes. From Fig. 6(a) it may be seen that the Debye–Waller factors associated with each scattering path increase as the bridging angle decreases. This increase can, in part, be attributed to a decrease in the frequency of the bending mode at these angles. The three scattering paths involving the second shell atom, however, show different degrees of sensitivity to the A_1 bend. The triple scattering path is the least sensitive since a change in the bridging angle does not appreciably change the length of the scattering path. The second shell single scattering path, however, is very sensitive to this bending mode since it induces a large change in the bromine–bromine distance. The double scattering path, on the other hand, is sensitive to both A_1 type modes. At low bridging angles the A_1 bend dominates primarily due to the low frequency of this mode when compared to the A_1 stretch at these angles. As the system approaches linearity the frequencies of both A_1 modes become comparable but the displacement vectors in the bending mode tend to become orthogonal to the internuclear axes. In such instances the A_1 stretch dominates the double scattering Debye–Waller factor.

The temperature dependence of the double and triple scattering Debye–Waller factors is shown in Fig. 6(b). The second shell single scattering factor [which is not shown in Fig. 6(b)] has the most severe temperature dependence due to the large contribution of the bending mode to this Debye–Waller factor. As described previously in I, the double and triple scattering factors are equal in magnitude at all temperatures when the bridging angle is 180°. At high temperatures and low bridging angles the double scattering factor is dominant. This occurs because the double scattering factor receives a large contribution from the A_1 bend which is a low frequency mode at these small angles. The triple scattering factor, however, is dominated by the higher frequency stretching mode. As the bridging angle increases the double scattering Debye–Waller factors, like the triple scattering factor, become dominated by the stretching mode such that both factors exhibit the same temperature dependence in the limiting case of a linear system.

The hyperbolic sine terms reflect the degree of correlation that exists between a change in scattering pathlength and a change in scattering angle. Figure 7(a) shows both the double and triple scattering hyperbolic sine terms together with the angular damping factor which is the exponent of the exponential term which represents the damping of the EXAFS due solely to a change in scattering angle. As described in the previous section, we shall only consider changes in the scattering angle α. Note that both the hyperbolic sine terms and the exponential damping term are dependent on the bond distance r_j. The magnitude of the hyperbolic sine terms is inversely proportional to the bond distance [see Eq. (14)]. The angular damping factor varies inversely as the bond distance squared. Throughout the present discussion a bond distance of 2.0 (Å) is assumed. Since the magnitude of each hyperbolic sine term may be approximated by its arguments at these angles, the effect of a change in bond distance may be readily calculated. Note also that the argument of the hyperbolic sine terms increase linearly with k while the angular damping factor is independent of k.

An understanding of the functional form of the hyperbolic sine terms requires a knowledge of the degree of correlation that exists, within each normal mode, between a change in distance and a change in scattering angle. On the basis of qualitative consideration we may conclude that a positive correlation exist in the A_1 stretching mode; that is, an increase in the scattering path length is accompanied by an increase in the scattering angle α (see Fig. 3). In the A_1 bend mode a negative correlation exists whereby an increase in the path length results in a decrease in the scattering angle α. Both of these conclusions are confirmed by a rigorous normal mode analysis. Since the A_1 bend contributes significantly to the double scattering Debye–Waller factor, the total correlation due to both A_1 modes represented by the double scattering hyperbolic sine term, is negative. The triple scattering hyperbolic sine term is positive, however, due to the dominant contribution of A_1 stretch which has a positive correlation. Note that for comparison purposes both the double and triple scattering hyperbolic sine terms are shown to be positive in Fig. 7. From Fig. 7(a) it may be seen that the magnitudes of both the double and triple scattering hyperbolic sine terms decrease rapidly as the system approaches linearity. This behavior may be readily explained in terms of the normal modes of a linear symmetric system. In this configuration the displacement vectors in the stretching mode produce no change in the scattering angle α. The displacement vectors of the atoms in the bending mode, however, produce a large change in α, but there is no change in dis-

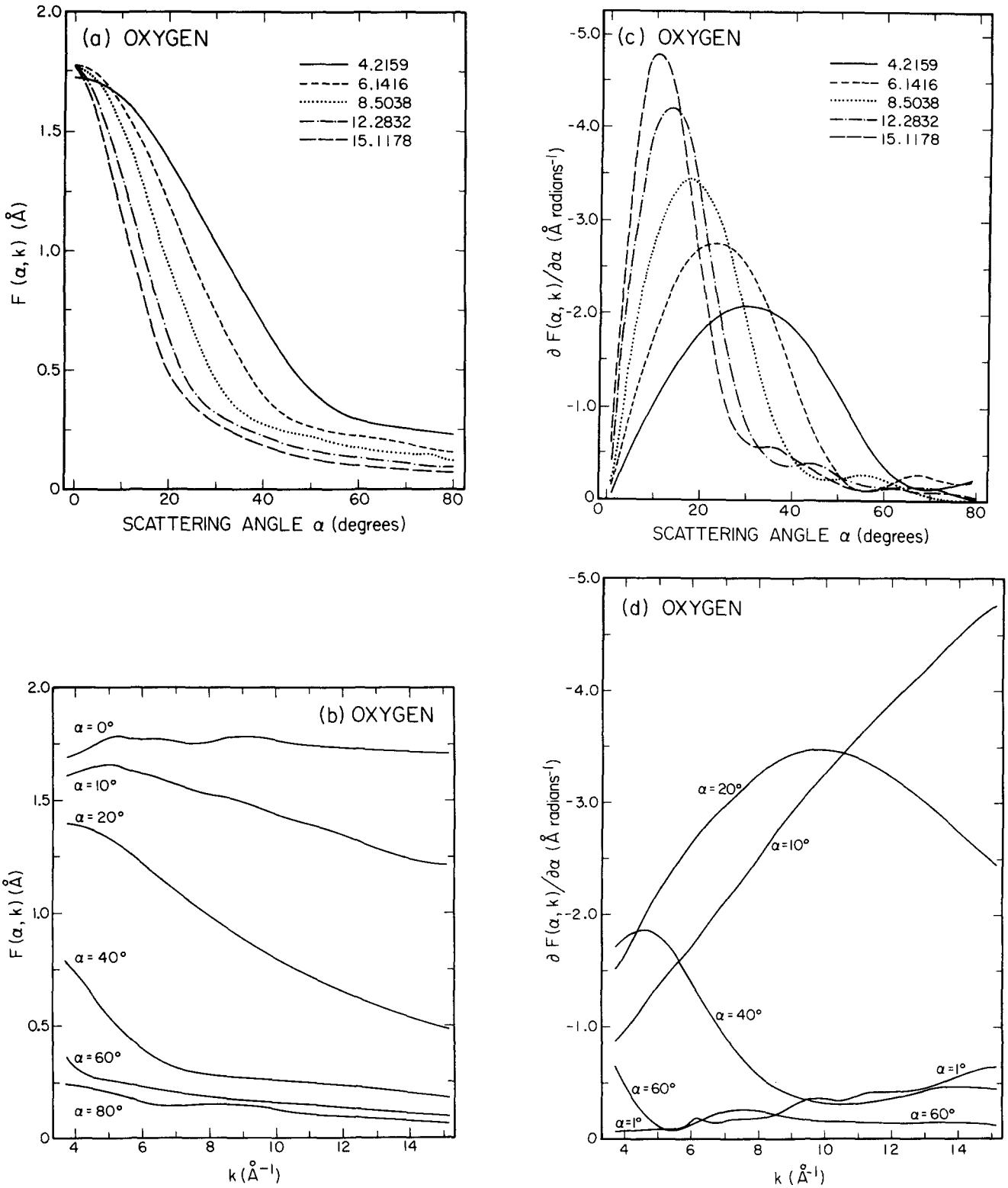
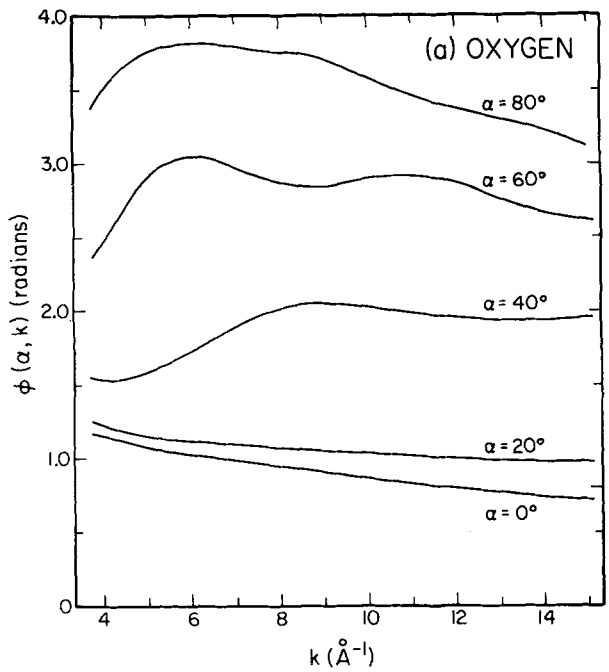
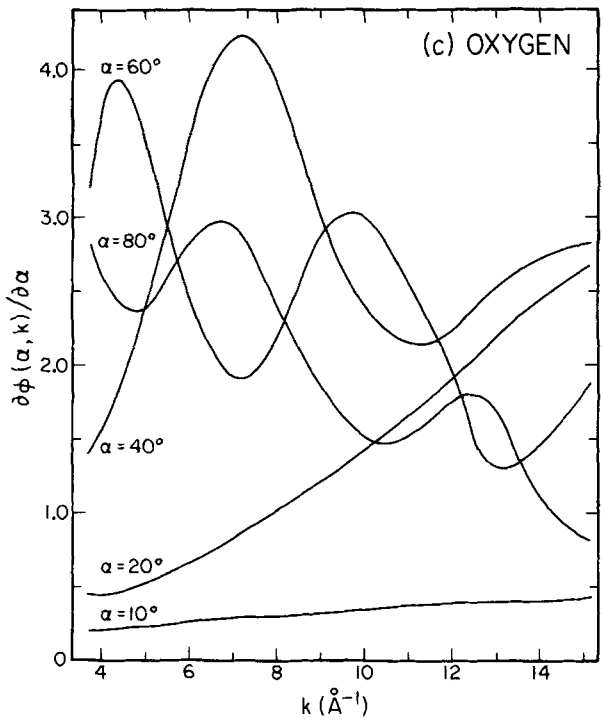


FIG. 8. Modulus of the scattering amplitude for oxygen. (a) As a function of scattering angle for various k values. (b) As a function of k for various scattering angles. (c) Rate of change of the modulus as a function of scattering angle for various k values. (d) Rate of change as a function of k for various scattering angles α.

tance as these vectors are orthogonal to the molecular axis. Therefore, both the double and triple hyperbolic sine terms tend to zero as the bridging angle of the system approaches 180°.

The angular damping factor increases as the three-atom system becomes less bent [see Fig. 7(a)]. As the bridging angle increases the contribution to this factor from the bending mode also increases. This occurs because the displacement vectors of the atoms in this mode tend to move increasingly perpendicular to the internuclear axes thereby inducing large changes in the scattering angle. The change in this angular damping factor as a function of angle is slow since the





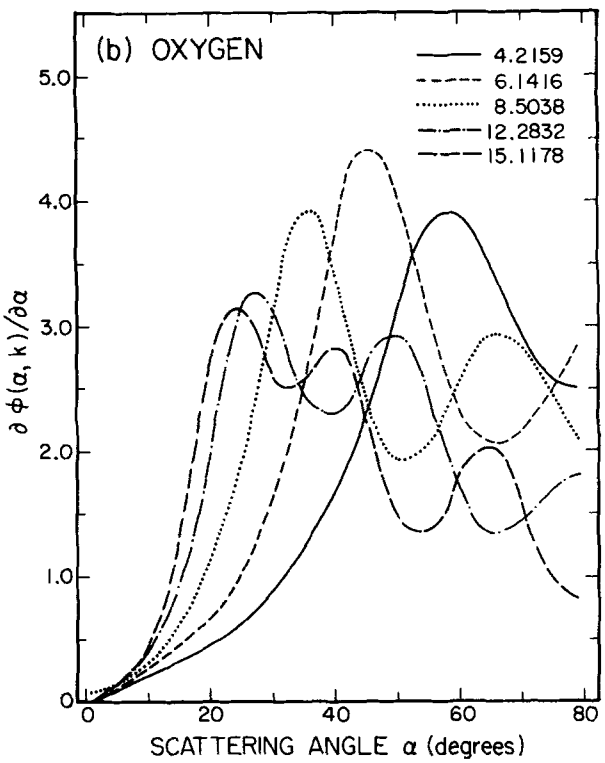
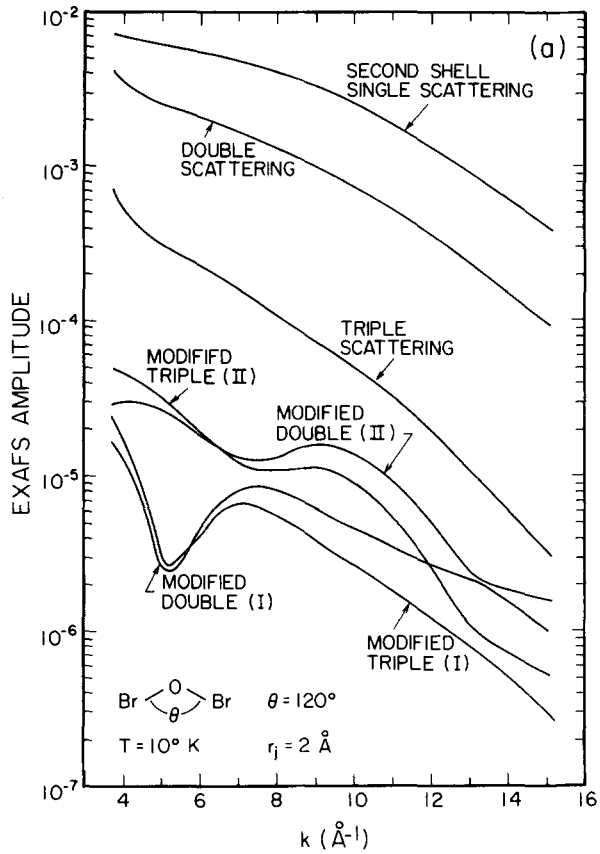
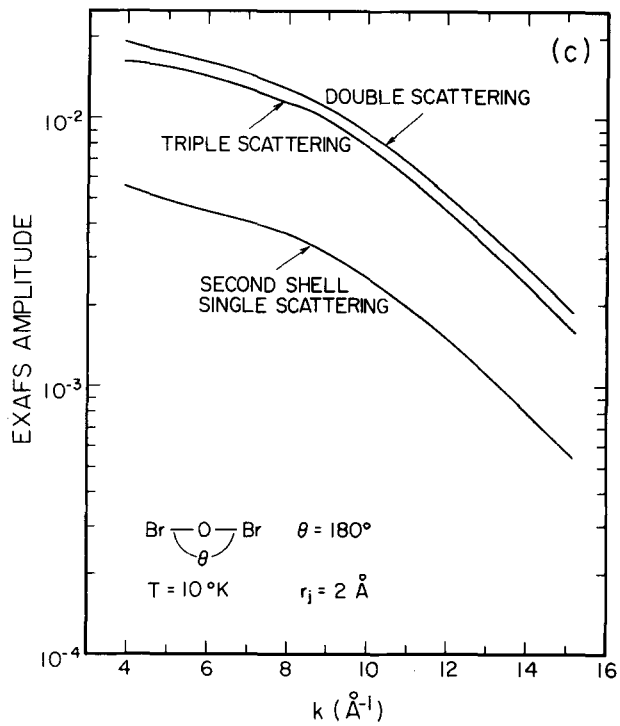


FIG. 9. Phase of the scattering amplitude for oxygen (a) as a function of k for various scattering angles α. (b) Rate of change of the phase as a function of scattering angle for various k values. (c) Rate of change as a function of k for various scattering angles α.

frequency of the bending mode increases as the bridging angle increases.

The temperature dependence of the double and triple scattering hyperbolic sine terms together with the angular damping factor is shown in Figs. 7(b)–(d). Note that the magnitude of the triple scattering hyperbolic sine term decreases with increasing temperature. The negative correlation due to the A_1 bend increases as the temperature rises thereby increasing the contribution of this mode to the hyperbolic sine terms. The contribution of the stretching mode also increases, but less sharply since the frequency of the stretch is greater than that of the bend. Since the total correlation of the triple scattering path is positive an increase in temperature only serves to reduce the magnitude of the correspond-





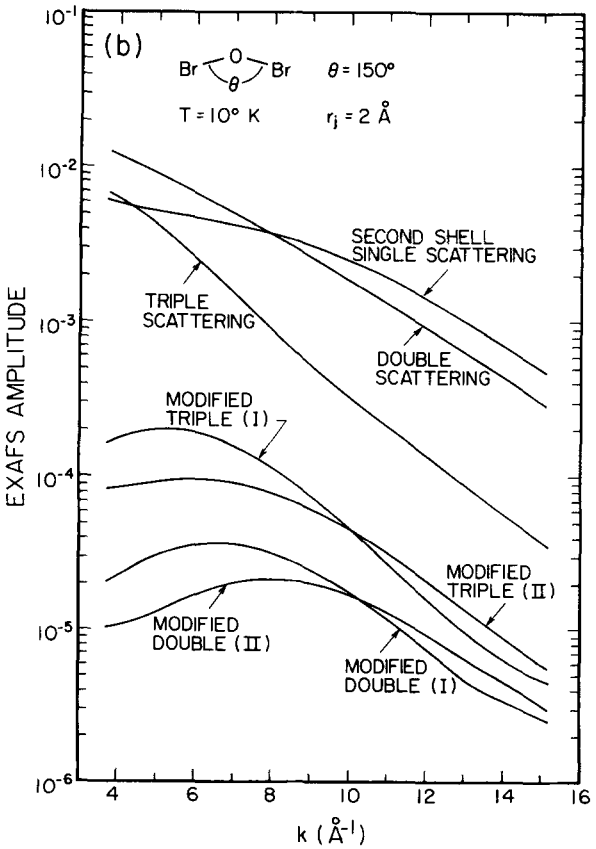


FIG. 10. Amplitude of the individual terms which contribute to the EXAFS of the Br_2O system. All calculations were carried out at 10 K and a bond distance of 2.0 Å. The sign of the modified triple scattering type I and II terms is positive while all other terms are negative. Note that the modified type I terms are to be multiplied by a cosine of the appropriate argument while the type II terms are multiplied by a sine. Amplitudes as a function of k are given for bridging angles of (a) 120° (b) 150°, (c) 180°.

ing hyperbolic sine term. The opposite, of course, is true in the case of the double scattering term where the existing negative correlation is further enforced by an increase in temperature.

The modulus and phase of the scattering amplitude for oxygen as a function of scattering angle and k are shown in Fig. 8 and Fig. 9. All calculations in these figures are based on the reported values of the amplitude and phase.[10] A detailed description of these functions has been given by Teo.[5]

Figure 8(a) shows the modulus of the scattering amplitude for oxygen as a function of scattering angle for a series of k values. In this angular range, the modulus is well described by the Born amplitude for the scattering of fast electrons off atoms. The modulus in the forward direction is independent of k and becomes increasingly peaked in the forward direction at higher k values. Outside this angular range, however, the modulus tends to develop complex structure which is related to the sampling of the oxygen core by the photoelectron. Figures 8(c) and 8(d) show the derivative of the modulus with respect to scattering angle as a function of k and scattering angle. Since the modulus has a local maximum at $\alpha = 0°$ [see Fig. 8(a)] the derivative is zero at this angle for all energies. Note that the sign of the derivative is negative while the derivative itself peaks at increasingly smaller scattering angles as the photoelectron wave number increases.

The phase of the scattering amplitude for oxygen as a function of k and a series of scattering angles is shown in Fig. 9(a). The derivative of the phase with respect to scattering angle as a function of scattering angle and k are shown in Figs. 9(b) and 9(c), respectively. The sign of the derivative is positive at all scattering angles. The magnitude of the derivative is small in the near forward scattering direction but becomes appreciable at larger scattering angles and shows complex structures as a function of k and scattering angle. The peaks which occur in the derivative of the phase occur at smaller scattering angles as the photoelectron wave number increases. In addition, subsidiary maxima occur at larger scattering angles, the number of such maxima increases at higher k values.

Before discussing the contribution to the observed EXAFS due to the various amplitude terms described above, we must consider the effect these terms have on the phase of the EXAFS oscillations. As described in the previous sections [see Eq. (22)] the phase of the oscillations in the modification factors is shifted by $\pi/2$ when compared to the oscillations of the original EXAFS. From Eq. (30) the derivative of the scattering amplitude in each modification factor may be written as

$$\left(\frac{\partial f_j(\alpha',k)}{\partial \alpha'}\right)_\alpha = e^{i\phi(\alpha,k)}\left(\frac{\partial F_j(\alpha',k)}{\partial \alpha'}\right)_\alpha + iF_j(\alpha,k)\,e^{i\phi(\alpha,k)}\left(\frac{\partial \phi(\alpha',k)}{\partial \alpha'}\right)_\alpha \quad (32)$$

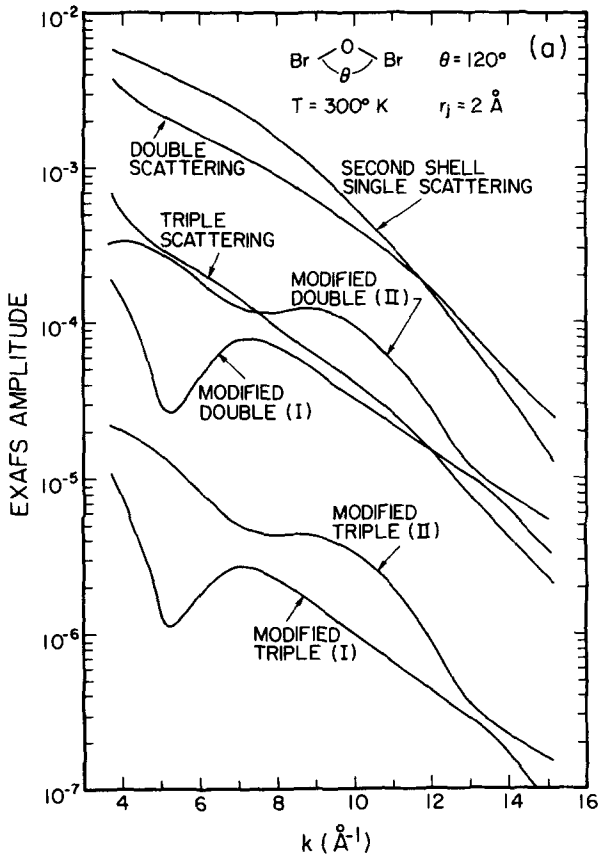
The first term on the right-hand side of Eq. (32) yields EXAFS oscillations that are shifted $\pi/2$ form the original. We shall refer to such terms as type I modification factors. The remaining term on the RHS gives rise to EXAFS oscillations that are π out of phase with the original and are called type II modification factors. Note that these latter factors serve to reduce directly the amplitude of the associated original EXAFS oscillations.

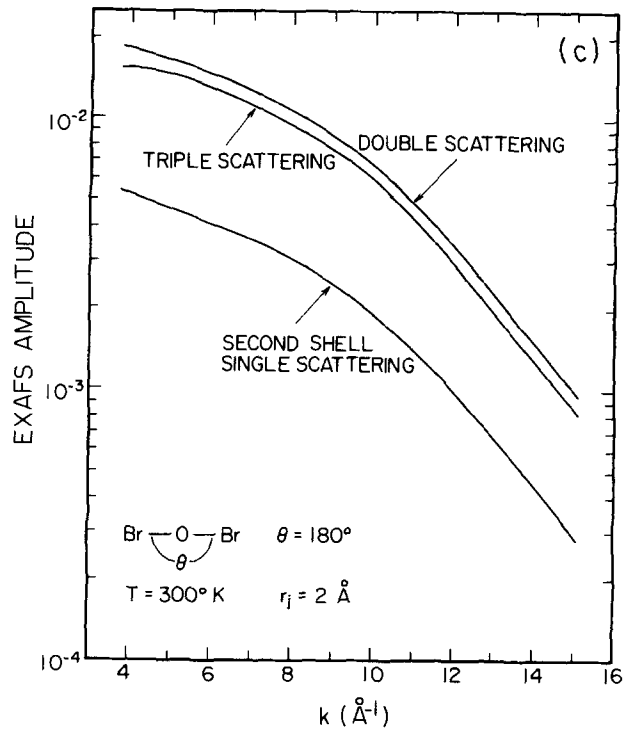
The amplitudes of the EXAFS oscillations for each scattering path including the associated modification factors are shown in Figs. 10 and 11. The amplitudes are calculated at three bridging angles and two temperatures. The parametrizations of Teo *et al.*[13] and Lee *et al.*[14] were used to describe modulus and phase of the backscattering amplitude for bromine. No damping terms reflecting the finite mean-free path of the photoelectron have been included in these calculations. Since the double scattering hyperbolic sine term is negative and the derivative of the amplitude is also negative, the double scattering type I modification factor remains $\pi/2$ out of phase with respect to original double scattering EXAFS oscillations [see Eqs. (23) and (32)]. However, since the derivative of the phase is positive the double scattering type II modification factor is exactly in phase with the original double scattering EXAFS oscillations. The triple scattering modification factors have exactly the opposite behavior since the associated hyperbolic since term is always positive. Thus the triple scattering type I modification factor is $3\pi/2$ out of phase while the type II factor is exactly out of phase with the original triple scattering EXAFS oscillations.

Figure 10 shows that the amplitude of the second shell single scattering EXAFS component increases gradually as the bridging angle increases. This increase is more pronounced at high k values and reflects the angular dependence of the Debye–Waller factor for this scattering path [see Fig. 6(a)]. The amplitudes of the double and triple scattering EXAFS components show a more dramatic increase with bridging angle and reflect a decrease in the Debye–Waller factor for these scattering paths together with an increased amplitude for scattering through small angles [see Fig. 8(a)]. At sufficiently large bridging angles the amplitudes of the double and triple scattering paths surpass that of the single scattering path.

The amplitudes of the modification factors are also shown in Fig. 10. The detailed structure observed in these factors may be attributed to the complex structures present in the amplitude and phase and their derivatives. The triple scattering modification factors increase in magnitude as the bridging angle increases due to the presence of the oxygen scattering amplitude which is absent in the corresponding double scattering factors [see Eq. (33)]. Furthermore, the triple scattering hyperbolic sine term falls off more gradually than the double scattering term as the bridging angles increase [see Fig. 7(a)]. In general, the magnitude of each modification factor is substantially smaller than that of the original damped EXAFS. When the bridging angle is 180° the amplitude of each modification factor is zero since both the correlation terms and the derivative of the scattering amplitude are zero at this angle.

A comparison of Figs. 10 and 11 reveals the temperature dependence of the EXAFS amplitude factors. Note that the magnitude of the second shell single scattering component is greatly diminished at higher temperatures. This is due primarily to the large dependence of this scattering path





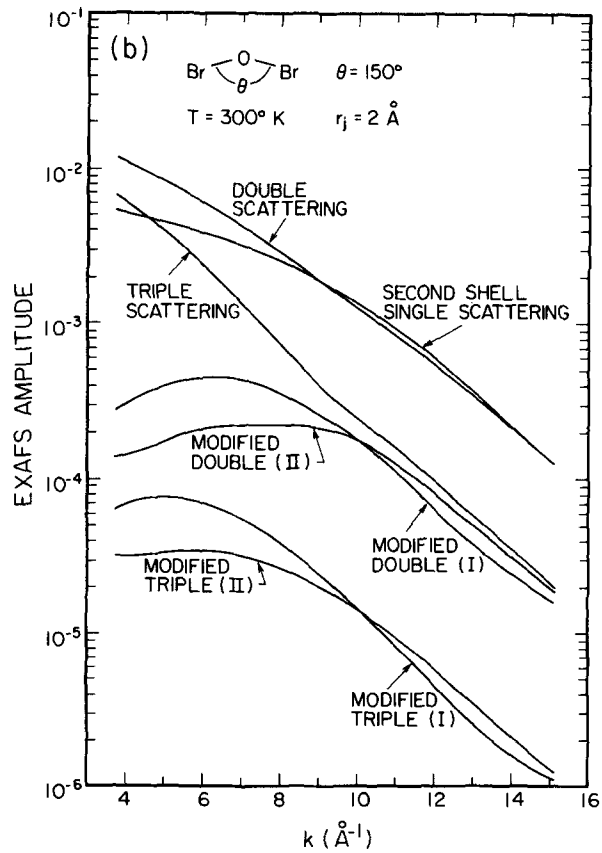


FIG. 11. Same as for Fig. 10 except that all calculations are for a temperature of 300 K.

on the low frequency bending mode of vibration. The magnitude of the double and triple scattering components exhibit a less severe temperature dependence. The double and triple scattering modification factors show different temperature dependences. Both double scattering modification factors increase with temperature while the triple scattering factors decrease. As described earlier, the double scattering modification factors serve to increase the total amplitude of the

double scattering EXAFS. The triple scattering modification factors, however, reduce the total triple scattering amplitude. Therefore in general, the contribution to the total EXAFS due to the modification factors of both the double and triple scattering paths increase as the temperature increases.

Recently Alberding and Crozier[7] introduced an integrated multiple-scattering (IMS) approach which explicitly considered variations in the scattering angle α. The authors, however, failed to recognize that such angular variations are a second order effect and to lowest order only distance variations are important [see Eqs. (9) and (10)]. Furthermore, these second order terms are negligible due to a lack of correlation (particularly in the forward direction) between changes in the scattering path length and the angle α. Accordingly, we feel the physical basis for this approach is unclear. The authors[7] also introduced a mean multiple scattering (MMS) approach to the analysis of EXAFS data. The failure of this latter approach to yield satisfactory results is discussed in I.

In conclusion, a change in the scattering angle α, induced by thermal vibrations, produces a large change in the scattering amplitude, particularly in the near forward direction. However, the correlation that exists between such an angle change and the associated change in distance for a given scattering path is small, especially at large bridging angles. It is the degree of correlation which determines the contribution of the modification factors to the observed EXAFS. Since the degree of correlation is small the modification factors may be neglected in an analysis of multiple scattering EXAFS data. Accordingly, for systems of this type it is sufficient to use the multiple scattering analysis proposed by Teo[5] provided an adequate treatment is given to the Debye–Waller factors which involve a change in scattering path length.[8]

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